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(21) International Application Number: PCT/EP98/01640 (22) International Filing Date: 20 March 1998 (20.03.98) (30) Priority Data: 03/832,167 2 April 1997 (02.04.97) US (71) Applicant (for all designated States except MN): ARCO CHEMICAL TECHNOLOGY, L.P. [US/US]; Two Greenville Crossing, Suite 238, 4001 Kenneth Pike, Greenville, DE 19807 (US). (71) Applicant (for MN only): ARCO CHEMIE TECHNOLOGIE NEDERLAND B.V. [NL/NL]; Theemsweg 14, NL-3197 KM Botlek Rotterdam (NL). (72) Inventors: COMBS, George; 245 Donofrio Drive, Downing- town, PA 19335 (US). McDANIEL, Kenneth, G.; 1005 Pine Valley Circle, West Chester, PA 19382 (US). (74) Agent: SMAGGASGALE, Gillian, Helen; Mathys & Squire, 100 Gray's Inn Road, London WC1X 8AL (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: POLYOXYALKYLENE MONOETHERS WITH REDUCED WATER AFFINITY (57) Abstract <p>Oleophilic polyoxyalkylene monoethers having reduced water affinity are disclosed. The monoethers have a hydrocarbyl residue, a polyoxyalkylene moiety, and a hydroxyl end group. The monoethers contain less than about 6 mole percent of alkoxylated unsaturates, and preferably less than about 5 mole percent of polyoxyalkylene diols. The monoethers offer substantial advantages for fuel compositions, particularly reduced water affinity. By using deposit-control additives based on the monoethers, formulators can offer better fuels for cleaner engines.</p>		

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POLYOXYALKYLENE MONOETHERS WITH REDUCED WATER AFFINITY

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FIELD OF THE INVENTION

The invention relates to polyoxyalkylene monoethers. In particular, the invention relates to polyoxyalkylene monoethers with reduced water affinity that have value as components of fuel additive detergent systems:

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BACKGROUND OF THE INVENTION

Polyoxyalkylene monoethers and their derivatives are well known and are widely used as components of fuel additive detergent systems to maintain the cleanliness of intake systems in internal combustion engines. Many traditional detergent systems have two components: (1) a polyoxyalkylene component, which acts as a carrier; and (2) a detergent. A wide variety of detergents are known, including carbamates, succinates, amine polyethers, and polyisobutylene amines (PIB amines). Examples of such two-component systems are those shown in U.S. Pat. Nos. 5,298,039 and 4,877,416. More recently, one-component detergent systems that incorporate a polyoxyalkylene moiety and a detergent function into a single polymer backbone have surfaced (see, for example, U.S. Pat. Nos. 5,427,591 and 5,600,025).

Polyoxyalkylene monoethers used as fuel additives must be oleophilic to be compatible with gasolines and the lipophilic detergents used to discourage or eliminate deposit formation. To achieve good solubility in and compatibility with fuels, polyoxyalkylene components are typically terminated with C₄-C₆₀ (more preferably C₉-C₃₀) hydrocarbyl (alkyl, aryl, or aralkyl) groups as described, for example, in U.S. Pat. Nos. 5,298,039, 4,877,416, and 4,422,856. Even with the hydrocarbyl groups present, the polyoxyalkylene components can be hydrophilic enough to form emulsions on contact with water in the fuel, or to phase separate from other hydrocarbon components.

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To enhance oil-solubility of polyoxyalkylene monoethers, formulators increase the oleophilic nature of the initiator alcohol (see, e.g., U.S. Pat. Nos. 5,298,039 and 5,600,025) or incorporate relatively hydrophobic oxyalkylene units such as those derived from C₄ epoxides (see, e.g., U.S. Pat. No. 5,004,478) or branched C₁₁-C₁₄ epoxides (see, e.g., U.S. Pat. No. 4,274,837). Unfortunately, these modifications are often more costly than desirable.

Polyoxyalkylene monoethers normally contain relatively minor amounts of polyoxyalkylene diol impurities. These diol impurities result from base-catalyzed polymerization of alkylene oxides, e.g., propylene oxide, in the presence of water, which acts as a starter for the polymerization. The diols lack the hydrocarbyl moiety of the monoethers. Until now, these minor amounts of diol impurities were not believed to adversely affect the performance of polyoxyalkylene monoethers in fuels.

Polyoxyalkylene monoethers made with C₃ and higher alkylene oxides contain a second type of impurity: alkoxylated unsaturates. A side reaction complicates base-catalyzed polymerization of many alkylene oxides: some of the alkylene oxide isomerizes to an allylic alcohol and other unsaturates under the reaction conditions. For example, propylene oxide isomerizes to allyl alcohol under basic conditions. Reaction of the allylic alcohol with the alkylene oxide gives alkoxylated unsaturates. While these impurities are "monoethers," they lack a relatively hydrophobic end group. Until now, these alkoxylated unsaturates, usually propoxylated allyl alcohols, were not believed to adversely affect the performance of polyoxyalkylene monoethers in fuels.

SUMMARY OF THE INVENTION

The invention is an oleophilic polyoxyalkylene monoether. The monoether has the structure:



wherein A is an oxyalkylene group, Z is a hydrocarbyl residue selected from the group consisting of C₄-C₆₀ alkyl, aryl, and aralkyl, and n, which is the average number of oxyalkylene groups, is within the range of about 2 to about 500. The monoether contains less than about 6 mole percent of
5 alkoxyated unsaturates, and preferably less than about 5 mole percent of polyoxyalkylene diols.

We surprisingly found that polyoxyalkylene monoethers containing less than about 6 mole percent of alkoxyated unsaturates offer substantial advantages for fuels. In particular, the monoethers have reduced water
10 affinity and a substantially reduced tendency to form emulsions with water present in lipophilic systems. These advantages of the monoethers suggest better fuel solubility. We also surprisingly found that reducing the content of polyoxyalkylene diol impurities in the monoethers to less than about 5 mole percent offers similar advantages. By using deposit-control
15 additives based on polyoxyalkylene monoethers of the invention, fuel formulators can offer better solutions for cleaner engines.

DETAILED DESCRIPTION OF THE INVENTION

Oleophilic polyoxyalkylene monoethers of the invention have the
20 general structure Z—(A)_n—OH, in which A is an oxyalkylene group, Z is a hydrocarbyl residue, and n is the average number of oxyalkylene groups.

Suitable oxyalkylene groups (A) result from ring-opening polymerization of one or more epoxides, including, for example, propylene oxide, butene oxides, pentene oxides, and the like. Preferably, the
25 polyoxyalkylene moiety of the monoether comprises recurring units derived from at least 50 mole percent of propylene oxide, up to about 49 mole percent of butene oxides, and not more than about 10 mole percent of ethylene oxide. Particularly preferred are polyoxyalkylene monoethers in which all of the oxyalkylene units are oxypropylene. The polyoxyalkylene
30 moiety can include a random configuration of oxyalkylene units, or it can be

a block copolymer.

The average number of oxyalkylene groups in the monoether, which is represented by "n" in the formula, is within the range of about 2 to about 500. For preferred monoethers, n is within the range of about 5 to about 100. More preferred is the range from about 10 to about 30; most preferred is the range from about 10 to about 25.

The monoethers include a hydrocarbyl residue (Z). The hydrocarbyl residue is a C_4 - C_{60} , more preferably a C_9 - C_{30} , alkyl, aryl, or aralkyl group. The hydrocarbyl residue is generally derived from a monohydroxy compound (e.g., an alcohol or phenol), which is a starter for an epoxide polymerization to make the polyoxyalkylene monoether. Particularly preferred are monoethers that derive from phenols substituted with C_4 - C_{15} alkyl groups, e.g., nonylphenol, and monoethers that derive from C_{10} - C_{20} , more preferably C_{12} - C_{15} , aliphatic alcohols. Examples of generally suitable structures for the polyoxyalkylene monoether appear in U.S. Pat. Nos. 4,234,321, 4,288,612, and 5,600,025, the teachings of which are incorporated herein by reference. Suitable hydrocarbyl residues include "pinwheel" type oxyalkylated alkylphenols such as those described in U.S. Pat. No. 5,600,025.

Polyoxyalkylene monoethers are normally made by basic catalysis, and consequently, they include significant concentrations of alkoxyated unsaturates, typically propoxylated C_3 unsaturates. Until now, these impurities were not believed to adversely affect the performance of polyoxyalkylene monoethers in fuels. We surprisingly found, however, that the concentration of alkoxyated unsaturates is important, and that polyoxyalkylene monoethers that contain less than about 6 mole percent of the alkoxyated unsaturates offer substantial advantages for fuels, including reduced water affinity and a reduced tendency to emulsify with water in lipophilic systems. More preferred polyoxyalkylene monoethers contain less than about 3 mole percent of alkoxyated unsaturates; most

preferred are monoethers having less than about 1.5 mole percent of alkoxyated unsaturates.

While there are several ways known in the art for making polyether compositions having very low concentrations of alkoxyated unsaturates (i.e., less than about 6 mole percent), a particularly valuable way is to make the polyoxyalkylene component using a double metal cyanide (DMC) catalyst. Suitable DMC catalysts, methods for their manufacture, and procedures for using them to catalyze epoxide polymerizations are described in U.S. Pat. Nos. 3,278,457, 3,941,849, 4,472,560, 5,158,922, 5,470,813, 5,482,908, the teachings of which are incorporated herein by reference. Particularly preferred are polyoxyalkylene monoethers prepared using substantially non-crystalline varieties of double metal cyanide catalysts, since those catalysts tend to give polymers with the lowest levels of alkoxyated unsaturates, typically less than about 3 mole percent, and often less than about 1.5 mole percent.

Preferred polyoxyalkylene monoethers also contain less than about 5 mole percent of polyoxyalkylene diols. Because the alcohol and phenol starters used to make polyoxyalkylene monoethers normally contain appreciable concentrations of water, base-catalyzed alkoxylation of the starter gives the desired monoether, but also gives a significant proportion of polyoxyalkylene diol resulting from epoxide polymerization with water as a starter. Until now, these diol impurities were not believed to adversely affect the performance of polyoxyalkylene monoethers in fuels. We surprisingly found, however, that the concentration of polyoxyalkylene diols is important, and that polyoxyalkylene monoethers that contain less than about 5 mole percent of the diols offer the advantages for fuels described earlier of using monoethers having a low content of alkoxyated unsaturates: reduced water affinity and a reduced tendency to emulsify with water in lipophilic systems. More preferred polyoxyalkylene monoethers contain less than about 2 mole percent of polyoxyalkylene diols.

To produce a polyoxyalkylene monoether having less than about 5 mole percent of polyoxyalkylene diols usually requires vacuum stripping of the starter molecule (alcohol or phenol derived from the hydrocarbyl moiety, Z) to reduce the water content of the starter. The stripping is usually performed at elevated temperature, preferably at a temperature within the range of about 60°C to about 200°C, more preferably from about 90°C to about 150°C. Purging the system with an inert gas such as nitrogen often helps to remove water. Azeotroping solvents (e.g., toluene, hexanes) can also be used to help strip out water. Before any epoxide is added to the starter and catalyst, the level of water in the starter is preferably less than about 5 mole percent.

As the results in Table 1 show, reduced water affinity results when the polyoxyalkylene monoethers contain low enough levels of diol and alkoxyated unsaturate impurities. When both diol and alkoxyated unsaturate contents are low, the tendency to form emulsions with water is relatively low. See Examples 1, 2, 5, and 7, in which the diol content is less than 5 mole percent, and the alkoxyated unsaturate content is less than 6 mole percent. Interfacial thickness, which is a measure of the monoether's tendency to form emulsions, is less than 5 mm in each case. In contrast, when the level of diol and/or alkoxyated unsaturate impurities is high (Comparative Examples 3, 4, and 6), the monoethers have a greater tendency to emulsify with water (interfacial thicknesses greater than 10 mm). The invention includes deposit-control additives based on the polyoxyalkylene monoethers. Two-component deposit-control additives of the invention comprise a detergent and the monoether. Suitable detergents are well-known in the art, and are described, for example, in U.S. Pat. Nos. 5,298,039 and 4,877,416, the teachings of which are incorporated herein by reference. Suitable detergents include, for example, carbamates, succinates, amine polyethers, polyisobutylene amines, and the like, and mixtures thereof. One-component deposit-control additives of

the invention incorporate a polyoxyalkylene moiety and a detergent function into a single polymer backbone. Examples of such one-component deposit-control additives appear, for example, in U.S. Pat. Nos. 5,427,591 and 5,600,025, the teachings of which are incorporated herein by reference.

The invention also includes fuel compositions made using the oleophilic polyoxyalkylene monoethers. The fuel compositions comprise a fuel and either a one-component or two-component deposit-control additive of the invention as described above. The fuel compositions may include other additives commonly known in the art, such as, for example, additional detergent additives, anti-knock agents; cetane enhancers, octane enhancers, and the like.

The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

EXAMPLE A

Preparation of a Polyoxypropylene Monoether from Nonylphenol

Nonylphenol (1006 g) is charged to a stainless-steel reactor. Zinc hexacyanocobaltate-tert-butyl alcohol complex (0.143 g, prepared as described in U.S. Pat. No. 5,482,908) is added, and the mixture is heated with stirring under vacuum at 130°C for 1 h to remove traces of water from the nonylphenol starter. Propylene oxide (4694 g) is introduced into the reactor over 6 hours. After the epoxide addition is complete, the mixture is heated at 130°C until no further pressure decrease occurs. The product is vacuum stripped and drained from the reactor.

EXAMPLE B

Preparation of a Polyoxyalkylene Monoether from a C₁₂-C₁₅ Propoxylate

The procedure of Example A is generally followed, except that a

C₁₂-C₁₅ fatty alcohol is used to initiate the polymerization. The amount of propylene oxide is adjusted to produce a monoether product having the desired number of oxypropylene (PO) units (see Table 1).

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EXAMPLE C

Measurement of Mole % Diols and Propoxylated C₃ Unsaturates

The mole % of polyoxyalkylene diols and propoxylated C₃ unsaturates reported in Table 1 are determined as follows. A polyoxyalkylene monoether sample is derivatized by reacting the hydroxyl groups in the sample with an excess of phthalic anhydride. The sample contains two kinds of "monols" (the desired polyoxyalkylene monoether and propoxylated C₃ unsaturates) in addition to polyoxyalkylene "diols." The hydroxyl groups in the sample are converted to phthalate half-esters, which have free -COOH groups. The relative amounts of diol and monols are then quantified by ion chromatography. Because the chromatography method does not distinguish between the two types of monols present, determination of the mole % of propoxylated C₃ unsaturates requires a second measurement. Polyol unsaturation, determined in the usual way by mercuric acetate titration, gives the mole % of monol due to the propoxylated C₃ unsaturates. Subtracting this value from the total mole % of monol as found by the chromatography method gives the mole % of polyoxyalkylene monoether.

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EXAMPLES 1-7

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Emulsification Testing for Water Affinity of Polyoxyalkylene Monoethers

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Generally, a modified version of ASTM method D-1094-96 is followed. Polyoxypropylene monoether samples (0.02 g) are combined with hexanes (3.6 g) in a screw-capped vial. The capped vial is swirled gently to completely dissolve the polyether. The cap is removed, and water (1.0 g) is added to the hexane solution. The vial is capped and shaken for

2 min. using a piston-like motion that traverses an arc of about 12 inches. The vial is shaken at 2-3 strokes per second for 2 min., and is then allowed to stand undisturbed for 5 min. A ruler is used to measure the height of the interfacial region (emulsified part) in mm after 5 min. and again after 30 min.

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Table 1. Emulsification Test Results: Polyoxypropylene Monoethers

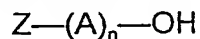
Ex. #	Mono-ether	# PO units	Diol (mole %)	C ₃ olefin (mole %)	Purity (%)	5 min. IF thickness (mm)	30 min. IF thickness (mm)
1	A	24	< 0.5	0.4	> 99	5.6	4.0
2	B	18	< 0.5	0.5	> 99	4.8	4.0
C3	C	24	1.4	12.4	86	13	9.5
C4	D	17	< 0.5	6.8	93	16	13
5	E	18	2.4	5.5	92	< 3.2	2.4
C6	F	19	9.0	11	80	16	15
7	G	18	3.0	0.6	96	4.0	3.2

A, B = C₁₂-C₁₅ alcohol-started; zinc hexacyanocobaltate-tert-butyl alcohol catalyst for propoxylation.
 C, D = C₁₂-C₁₅ alcohol-started; KOH catalyst for propoxylation.
 E, F = Nonylphenol-started; KOH catalyst for propoxylation.
 G = Nonylphenol-started; zinc hexacyanocobaltate-tert-butyl alcohol catalyst for propoxylation.
 IF = interfacial

The preceding examples are meant only as illustrations; the following claims define the scope of the invention.

We claim:

1. An oleophilic polyoxyalkylene monoether of the structure:



wherein A is an oxyalkylene group, Z is a hydrocarbyl residue selected from the group consisting of C₄-C₆₀ alkyl, aryl, and aralkyl, and n, which is the average number of oxyalkylene groups, is within the range of about 2 to about 500;

wherein the monoether contains less than about 5 mole percent of polyoxyalkylene diols and less than about 6 mole percent of alkoxyated unsaturates.

2. The monoether of claim 1 wherein A is oxypropylene.

3. The monoether of claim 1 wherein Z derives from nonylphenol.

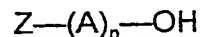
4. The monoether of claim 1 wherein Z derives from a C₁₂-C₁₅ aliphatic alcohol.

5. The monoether of claim 1 wherein Z is selected from the group consisting of C₄-C₃₀ alkyl, aryl, and aralkyl.

6. The monoether of claim 1 wherein n has a value within the range of about 10 to about 30.

7. The monoether of claim 1 containing less than about 2 mole percent of polyoxyalkylene diols and less than about 3 mole percent of alkoxyated unsaturates.

8. An oleophilic polyoxyalkylene monoether of the structure:



wherein A is an oxyalkylene group, Z is a hydrocarbyl residue selected from the group consisting of C₄-C₆₀ alkyl, aryl, and aralkyl, and n, which is the average number of oxyalkylene groups, is within the range of about 2 to about 500;

wherein the monoether contains less than about 5 mole percent of polyoxyalkylene diols.

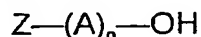
9. The monoether of claim 8 wherein A is oxypropylene.

10. The monoether of claim 8 wherein Z is selected from the group consisting of C₄-C₃₀ alkyl, aryl, and aralkyl.

11. The monoether of claim 8 wherein n has a value within the range of about 10 to about 30.

12. The monoether of claim 8 containing less than about 2 mole percent of polyoxyalkylene diols.

13. An oleophilic polyoxyalkylene monoether of the structure:



wherein A is an oxyalkylene group, Z is a hydrocarbyl residue selected from the group consisting of C₄-C₆₀ alkyl, aryl, and aralkyl, and n, which is the average number of oxyalkylene groups, is within the range of about 2 to about 500;

wherein the monoether contains less than about 6 mole percent of alkoxyated unsaturates.

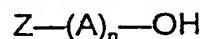
14. The monoether of claim 13 wherein A is oxypropylene.

15. The monoether of claim 13 wherein Z is selected from the group consisting of C₄-C₃₀ alkyl, aryl, and aralkyl.

16. The monoether of claim 13 wherein n has a value within the range of about 10 to about 30.

17. The monoether of claim 13 containing less than about 3 mole percent of alkoxyated unsaturates.

18. An oleophilic polyoxypropylene monoether of the structure:



wherein A is an oxypropylene group, Z is a hydrocarbyl residue selected from the group consisting of C₄-C₆₀ alkyl, aryl, and aralkyl, and n, which is the average number of oxypropylene groups, is within the range of about 10 to about 30;

wherein the monoether contains less than about 5 mole percent of polyoxypropylene diols and less than about 6 mole percent of propoxylated C₃ unsaturates.

19. The monoether of claim 18 containing less than about 2 mole percent of polyoxypropylene diols and less than about 3 mole percent of propoxylated C₃ unsaturates.

20. A one-component deposit-control additive that derives from the polyoxyalkylene monoether of claim 1.

21. A two-component deposit-control additive which comprises a detergent and the polyoxyalkylene monoether of claim 1.

22. A composition which comprises a fuel and the one-component deposit-control additive of claim 20.

23. A composition which comprises a fuel and the two-component deposit-control additive of claim 21.

24. A one-component deposit-control additive which derives from the polyoxyalkylene monoether of claim 13.

25. A two-component deposit-control additive which comprises a detergent and the polyoxyalkylene monoether of claim 13.

26. A composition which comprises a fuel and the one-component deposit-control additive of claim 24.

27. A composition which comprises a fuel and the two-component deposit-control additive of claim 25.

28. The monoether of claim 1 prepared using a double metal cyanide catalyst.

29. The monoether of claim 13 prepared using a double metal cyanide catalyst.

30. A method of reducing the water affinity of a fuel composition, said method comprising using as a fuel component the polyoxyalkylene monoether of claim 1.

31. A method for reducing the water affinity of a fuel composition, said method comprising using as a fuel component the polyoxyalkylene monoether of claim 13.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/01640

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G65/26 C10L1/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 962 237 A (LAYCOCK DAVID E) 9 October 1990 see claims 1,2,9 see column 2, line 29 - line 32 ----	13-17
X	EP 0 090 444 A (SHELL INT RESEARCH) 5 October 1983 see claims 1,15,16 see page 11, line 1 see page 1, line 11 ----	13-17, 24,29
X	US 3 941 849 A (HEROLD ROBERT JOHNSTON) 2 March 1976 cited in the application see claims 1,5 ----- -/-	13-17



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

30 June 1998

Date of mailing of the international search report

09/07/1998

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/01640

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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